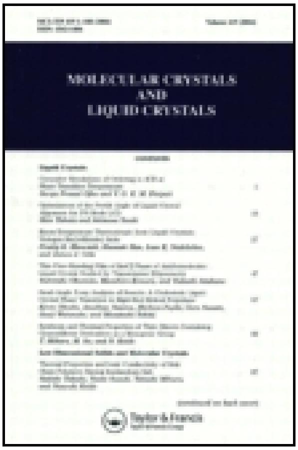

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Influence of Pyrolysis Conditions on the Performance of Hard Carbons as Anodes for Lithium Batteries

Elzbieta Frackowiak [a], Sophie Gautier [a], Fabrice Leroux [a], Jean-Noel Rouzaud [a] & Francois Beguin [a]

[a] CRMD, CNRS-Université, IB rue de la Férollerie, 45071, Orléans, France

To cite this article: Elzbieta Frackowiak, Sophie Gautier, Fabrice Leroux, Jean-Noel Rouzaud & Francois Beguin (2000): Influence of Pyrolysis Conditions on the Performance of Hard Carbons as Anodes for Lithium Batteries, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 431-436

To link to this article: http://dx.doi.org/10.1080/10587250008025505

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 431-436
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Influence of Pyrolysis Conditions on the Performance of Hard Carbons as Anodes for Lithium Batteries

ELZBIETA FRACKOWIAK, SOPHIE GAUTIER, FABRICE LEROUX, JEAN-NOEL ROUZAUD and FRANCOIS BEGUIN

CRMD, CNRS-Université, 1B rue de la Férollerie, 45071 Orléans, France

Electrochemical lithium insertion/deinsertion has been correlated with the pyrolysis parameters of a polymeric precursor, the microtexture and chemical composition of the obtained hard carbon. A specific reversible capacity of 450 mAh/g (i.e. composition $LiC_{4.5}$) has been estimated for the optimal carbons from the galvanostatic charge/discharge characteristics. Voltammetry experiments and galvanostatic relaxation curves demonstrated that lithium insertion/extraction process is not kinetically controlled by diffusion, for the current load (20 mA/g) and scan rate used for our experiments. The sites for lithium insertion and/or intercalation were estimated from ex-situ ^7Li NMR experiments for differently lithiated samples. A Knight shift of 60 ppm characteristic of lithium clusters has been found for carbons obtained under strains.

Keywords: hard carbon; two-step pyrolysis; carbon anode; lithium insertion; ^7Li NMR

INTRODUCTION

Optimal carbon materials for anode of Li-ion batteries must fulfil special criteria, such as a high reversible capacity for lithium storage, a lack of hysteresis between lithium insertion and extraction, a very limited self-discharge and a low irreversible capacity consumed for the decomposition of electrolyte and the formation of a solid electrolyte interphase (SEI). Tremendous work has been devoted for testing different carbonaceous materials (soft and hard) as potential materials for anodes.

Reversible lithium storage capacity of hard carbons ($Q_{rev.}$) has been often correlated with the final temperature of pyrolysis, the kind of precursor, the effect of milling or especially introduced oxygen, ...[1-3]. For the first time, we show in this paper that mechanical strains applied during two-step pyrolysis of an organic precursor can be profitable for improving Q_{rev}.

EXPERIMENTAL

Pyrolysis of films from a wood precursor at 450°C for two weeks and at 1000°C for a short time gave sample 1. Sample 2 was the result of heat-treatment at 450°C for 7 minutes and at 1000°C for 7 minutes under mechanical strains.

Electrochemical investigations have been performed in a two-electrode cell, where carbon was the working electrode and a lithium disk was simultaneously the counter and the reference electrode. The electrolyte used was 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC).

The galvanostatic investigations of the lithium/carbon cells were performed with a Mac Pile generator (Biologic, France) at 20 mA/g and in the potential range from 3 V to -0.020 V *vs* Li/Li^+, and for the potentiostatic experiments the voltage step was 10 mV/0.2h. The role of kinetics in the insertion/de-insertion process was estimated by the galvanostatic intermittent titration technique (GITT) with a charge of 0.05 Faraday per mole of 6C followed by 24 hours of relaxation.

The structure and the microtexture of the hard carbon films were characterized by high resolution transmission electron microscopy (TEM, Philips CM 20).

Nitrogen adsorption isotherms at 77K were investigated by Micromeritics ASAP 2010. Before adsorption the samples were outgassed at 350°C until the pressure reached a value of 10^{-4} mbar.

The carbon electrodes were examined at various steps of insertion/de-insertion by solid state ^7Li NMR (Brucker 360 spectrometer, frequency 139.9 MHz). The cell was relaxed one day after reaching the selected potential. Then, the electrode material was dried overnight in the glove box and sealed in a NMR probe for ex-situ experiments.

RESULTS AND DISCUSSION

Even if the final temperature for the pyrolysis was the same for the two samples, we detected small differences in the oxygen composition (Table I). The low oxygen content of sample 1 is attributed to the long pre-carbonization treatment at 450°C, which allows more important evolution of CO and H_2O.

TABLE I Elemental analyses (wt%) of the carbon samples

Sample	C%	H%	0%
1	93.5	0.6	1.4
2	93.2	0.6	3.8

Significant differences were detected in the TEM observations of the carbon films. The structure and the microtexture of sample 1 are typical of a hard carbon obtained at 1000°C. The basic structural units (BSU), made of stacks of 2-3 nanometric graphene layers, are strongly misoriented (Figure 1a). When mechanical strains are applied during the pyrolysis (sample 2), the size of graphene layers is more important and a mutual parallel organization of the BSU is visible with a tendency for the formation of nanometric slits (Figure 1b). However, in comparison with the microtexture of soft carbons (e.g. antracene coke), the preferential orientation of BSU is much less developed, as demonstrated by the non-graphitizability after heat treatment of sample 2 at 2800°C.

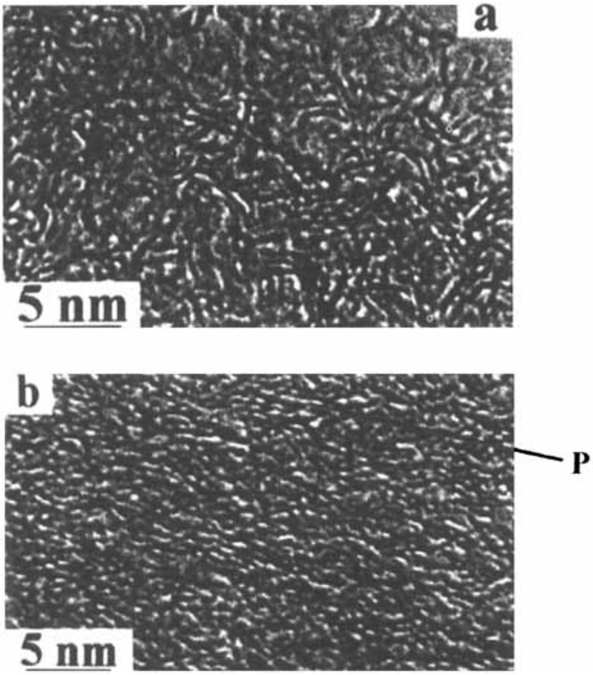

Figure 1. TEM images (002 lattice fringes) of: a) sample 1 (BSU at random); b) sample 2 obtained under strains (BSU preferentially oriented along P).

The nitrogen adsorption isotherms at 77K on both investigated carbon films confirmed the microporous character of these materials. The value of BET surface area was 260 m^2/g for sample 1, and 290 m^2/g for sample 2. From the t-plot dependence, the external surface area was calculated and it represented a negligible value of 0.2 m^2/g (sample 1) and 2 m^2/g (sample 2).

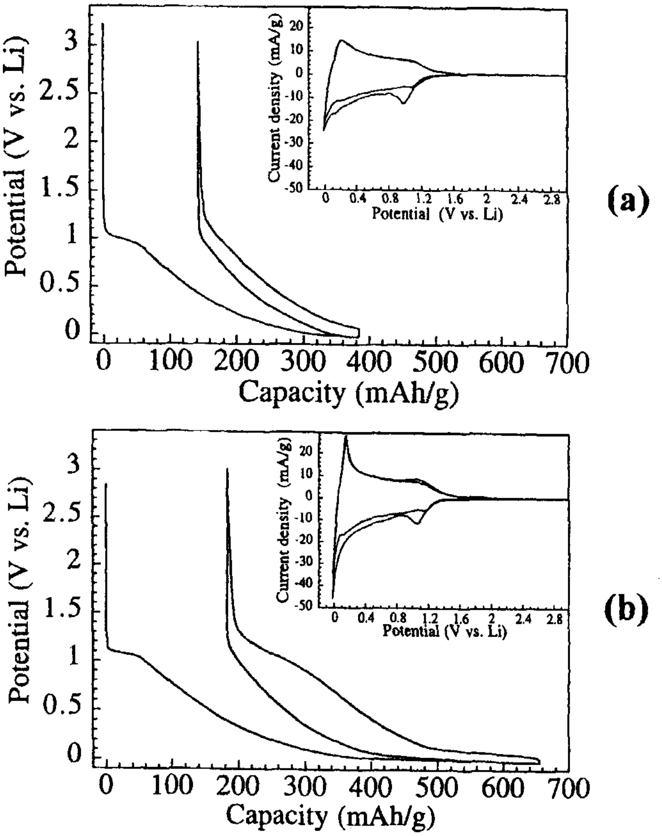

Figure 2. Li insertion/deinsertion at 20 mA/g: (a) sample 1; (b) sample 2. Insets: potentiostatic mode (10mV/0.2h).

The electrochemical behavior of the two hard carbon samples (without and under strains) is well illustrated in Figure 2. The galvanostatic profile of sample 2 is characterized by an extremely long plateau close to 0 V *vs* Li/Li$^+$. From the example of GITT experiment performed on sample 1 (Figure 3), it is clear that kinetic limitations play a negligible role for the small polarization between insertion and deinsertion of lithium. Additionally, the values of specific capacity obtained from the typical charge/discharge galvanostatic experiments at 20 mA/g and by the relaxation GITT experiments were the same, hence, in our experimental conditions the process of insertion and extraction of lithium is not controlled by the diffusion of Li$^+$. The reversible capacity for sample 2 reaches a high value of 450 mAh/g, which is definitively greater than in graphite (372

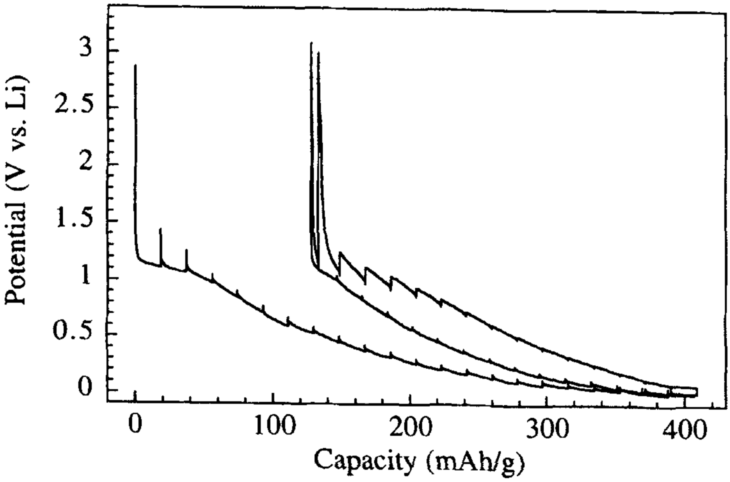

Figure 3. GITT experiments on sample 1

mAh/g for LiC_6). Well visible redox peaks close to 0 V *vs* Li/Li^+ in the voltammetric curves of sample 2 (Figure 2, inset) are the signature for a part of lithium intercalated between pseudo-graphitic layers. The value of irreversible capacity (from 140 to 180 mAh/g) is strictly connected with the surface area of carbons. It is noteworthy that at the high degree of lithium insertion, electroplating is definitively excluded in our experiments, as it was confirmed in ^{7}Li NMR experiments demonstrating the absence of a peak at the position expected for metallic lithium (262 ppm).

^{7}Li NMR spectra of sample 2 at different state of lithium insertion (0.4 V, 0.1 V and –0.020 V *vs* Li) are shown in Figure 4. The Knight shift of 60 ppm reached for the fully lithiated sample is greater than for LiC_6, confirming the existence of dense lithium islands. The values of shift during the removal of lithium differ moderately from the values found for insertion, that can be explained by the mobile Li sites or by the small polarization between these two processes.

Finally, the pyrolysis conditions exert an influence on the electrochemical characteristics of the investigated carbons. The oxygen content in the final product is related with the duration of pre-carbonization treatment. In this case, C-O-C ether bridges between BSU could favor the formation of slit-shape nanopores when mechanical strains are applied during carbonization. Such pores would be responsible for trapping lithium clusters. The more important polarisation observed for sample 2 is also attributable to the edge oxygenated groups which can present ion-dipole interaction with the inserted lithium ions.

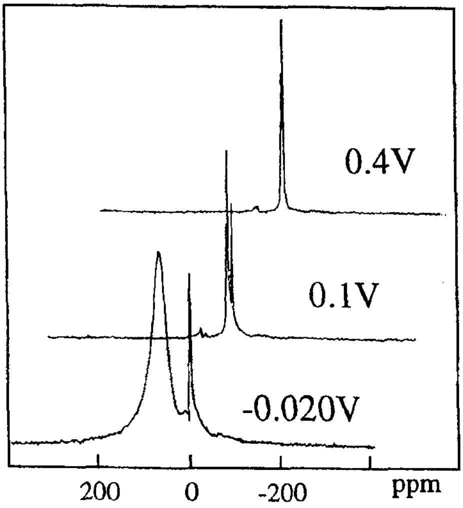

Figure 4. ^{7}Li NMR on sample 2 at various steps of lithiation

CONCLUSION

The pyrolysis parameters and the application of strains strictly determine the microtexture of hard carbon films even if the final temperature of treatment is the same (1000°C). The content of carbon and hydrogen in both carbons are comparable, the only slight difference is the amount of oxygen. The microtextural observation confirmed a different organization of the BSU with a possibility of nanometric slit-shape pores formed under the effect of the mechanical strains. The existence of C-O-C bridges can be responsible for additional accumulation of lithium. Different lithium sites such as: between pseudographitic layers (pure intercalation) and small clusters in the slit nanometric pores have been confirmed by ^{7}Li NMR and electrochemical experiments. The Knight shift of 60 ppm is the best proof for the dense lithium islands. A reversible capacity of 450 mAh/g ($LiC_{4.5}$) with a long potential plateau close to 0 V *vs* Li has been found.

References

[1] C.S. Wang, G.T. Wu and W.Z. Li, *J. Power Sources*, **76**, 1 (1998).

[2] F. Disma, L. Aymard, L. Dupont and J-M. Tarascon, *J. Electrochem. Soc.*, **143**, 3959 (1996).

[3] E. Peled, V. Eshkenazi, Y. Rosenberg, *J. Power Sources*, **76**, 153 (1998).